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THE THERMAL DEGRADATION OF AVIATION FUELS IN JET ENGINE INJECTOR FEED-ARMS:
RESULTS FROM A HALF-SCALE RIG

By

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INTRODUCTION

Aviation kerosine undergoes significant heating within the fuel system of an aviation gas turbine. Heating occurs because, firstly, fuel is used as a coolant for the engine lubricating oil and for other heat exchanger systems (e.g. avionics, air conditioning, etc.) and, secondly, because certain regions have a high intrinsic temperature (e.g. injector feed-arms). The feed-arms, which pass fuel directly into the combustor, represent the most severe fuel system environment in that the combination of high fuel inlet temperatures and very hot metal surface can promote a very high degree of thermal degradation. In this event, the small apertures within the fuel atomisers can become obstructed, causing flow restriction or fuel spray pattern distortion, and leading ultimately to engine malfunction. Thus, the thermal stability of aviation fuels within the feed-arm environment is crucial for the safe operation of gas turbine engines.

Whilst the thermal degradation of aviation fuels is well documented¹, relatively few researchers have addressed the specific problem of deposition within burner feed-arms²⁻⁴. Two such investigations were collaborative projects³⁻⁴ between Shell Research and Rolls-Royce plc., Derby. A full-scale rig simulation³, the IFAR (Injector Feed-Arm Rig), was used to look at the effects on fouling of fuel flow rate and fuel pressure, the addition of additives, and rig repeatability. However, the large appetite of the rig (50,000 litres of fuel per test) prevented a more detailed examination of the contribution of fuel chemistry to the fouling.

The study reported here used a half-scale rig, the MIFAR (Mini Injector Feed-Arm Rig), which is similar in design to the IFAR and operates at identical temperatures. The use of this scaled-down rig with its significantly decreased fuel appetite - a reduction from 50,000 litres to 2,000 litres/test - has enabled the effects of fuel processing and chemistry on feed-arm fouling to be evaluated for a wide range of fuels. In addition, it has permitted correlations to be drawn between the MIFAR and other thermal stability rigs.

The objectives of the research program were as follows:

- To make a direct comparison of fuel performance in large- and small-scale injector feed-arm rigs, and thence to pursue the initial findings about the feed-arm deposition process.

- To relate a fuel's deposition tendency to its chemical composition and to correlate the MIFAR with other predictors of fuel thermal stability, in particular to the JFTOT (Jet Fuel Thermal Oxidation Tester).
- To gain greater insight into the action of one additive, the approved metal deactivator, Du Pont's MDA, specifically to confirm related findings⁵ on its dual action as metal chelator and metal passivator.

EXPERIMENTAL

Mini Injector Feed-Arm Rig (MIFAR)

The philosophy underlying the aviation fuel thermal stability testing pursued at Shell Research Ltd has been always to construct simulation rigs, using actual engine components where possible, and to measure fuel deposition quantitatively at well characterised temperatures. The MIFAR, illustrated in Figure 1, is a realistic, half-scale simulation of an aircraft fuel system. Fuel is supplied from external storage tanks via a 0.45 μ m filter to a glass reservoir (to simulate a wing tank); in the current programme, the reservoir was left unheated to simulate the absence of fuel recirculation in civil aviation practice. On leaving the reservoir, the fuel is pressurised to 250 psi by a Lucas high-pressure piston pump and supplied to a fuel line heater, comprising two stainless-steel sheathed electrical cartridge heaters in series; the heaters simulate the avionic and engine cooling components of a gas turbine engine. The hot (165°C), pressurised fuel is then fed to a model feed-arm mounted in a fluidised sandbath, which simulates the hot compressor discharge air environment. Thereafter, the fuel passes through filters, is cooled and dumped to waste. A DEC micro PDP-11 computer provides automatic control of the rig operating conditions via process control software; the same software also provides data logging and reporting functions.

At Shell Research the model feed-arms are designed to simulate the burner stems that lead to the nozzle assemblies and are plain, thick-walled steel tubes (0.25" O.D. x 0.090" I.D.), corresponding to a half-scale system. The tubes are instrumented with thermocouples mounted in grooves along the arms to allow the temperature of the inner wall (TIW) to be measured. Only the central 10 cm of the arm (corresponding to 7.2 cm²) are immersed in the sandbath. Bulk fuel temperatures at the inlet and outlet of the arm are determined by the associated thermocouples.

Deposition Monitoring

The deposition process is monitored "on-line" during a test by measuring the rise in the inner wall temperature (Δ TIW) of the feed-arm; this rise occurs because of the deposit's insulating effect on heat transfer. After a test has been completed, the deposit mass is calculated from the amount of carbon (W_c) recovered as carbon dioxide from the controlled combustion of the deposit. Empirical data have shown that the weight of carbon recovered is 70% of the original deposit weight; this allows W_c values to be converted into deposit weight (W_d) values, thus providing an "off-line" reference of fouling rate.

Test conditions

As with the IFAR⁴, the tests were targetted to reflect severe thermal conditions; therefore a bulk fuel inlet temperature of 165°C and an inner wall temperature of 300°C were selected. The fuel pressure was 250 psi, and a flowrate of 300 ml/min was chosen to give a turbulent flow regime (Reynold's Number, $Re = 8000$).

The 300°C TIW was achieved by adjusting the temperature of the fluidised sandbath within the range 410°-450°C at the start of each test; thereafter the sand bath was maintained at a constant temperature.

Test fuels

The ten fuels studied included examples of the three main process types: sweetening, hydrotreating and hydrocracking. Most were Jet A/A-1 type fuels meeting the DERR 2494/ASTM D1655 specifications, but some were chosen because of their poor/borderline stability. The fuels and their inspection properties are listed in Table 1. The fuels encompass a wide range of sulphur contents and responses in the JFTOT specification thermal stability test. These fuels were used in a series of 16 tests (detailed in Table 2).

RELATED THERMAL STABILITY TESTS/RESULTS

Fuel performance within the MIFAR was not considered in isolation; the wide range of thermal stability tests available at Shell Research enabled fuel performance in the MIFAR to be compared with other measures of stability. From these data, two complementary pieces of information were derived: firstly, the ability of other tests to predict fuel performance - as determined in a realistic environment; secondly, the prediction of fuel performance from more fundamental compositional information.

The IFAR

The IFAR was built as part of a programme undertaken jointly by Shell Research and Rolls-Royce to study injector feed-arm fouling⁴. The rig, whilst similar in principle to the MIFAR, is essentially a full-scale simulation. The operating principles, test temperatures and measurements made are directly comparable and essentially identical to those of the MIFAR. Insights gained from the IFAR into feed-arm fouling have been published in the literature^{4,5}.

The single tube heat transfer rig (STHTR)

The STHTR realistically simulates fuel degradation within an oil-cooler⁶. It is Shell's principal benchmark of fuel thermal stability in service, insofar as it duplicates the dimensions, fuel flow rates and metallurgy of an oil-cooler. In the rig, the fuel undergoes three stages of heating to simulate those heat sources encountered in an aircraft fuel system:

- Fuel tank heating (aerodynamic heating, fuel transfer/recirculation)
- Heating from hydraulics/avionics/environmental system heat exchangers
- The engine oil-cooler (i.e., that component simulated by the test heat-exchanger)

Fuel degradation is monitored via the reduction in heat-transfer coefficient of the test element.

JFTOT testing

For commercial purposes, the thermal stability of aviation fuels is generally assessed in the Jet Fuel Thermal Oxidation Tester⁷ (JFTOT, ASTM method D3241) at a defined temperature. In essence, fuel is passed over a heated metal tube and then through a filter; the fuel is rated on a go/no go basis by the tube lacquer or the blockage of the filter. For research purposes this is not very informative. Accordingly, in the current work, fuels were ranked using the breakpoint temperature (i.e., the highest temperature sustainable without causing the fuel to fail on the tube lacquer or filter blockage criterion.) In addition, the degree of carbon deposition in the tests carried out at a 350°C tube temperature was also determined.

Flask oxidation studies

The flask oxidation test (FOT) is an in-house method of measuring the liquid phase oxidation rate of fuels and thereby determining their other oxidation characteristics⁸. Perturbing the system with a radical initiator (t-butyl peroxide) enables a fuel's intrinsic radical initiation rate to be determined. This rate has been found to be a good predictor of a fuel's deposition tendency within our oil-cooler simulation.

MIFAR RESULTS: DEPOSITION RATES

The raw MIFAR test results comprise two types of measurement:

- (i) The tube wall temperature, TIW, recorded as a function of time throughout the test;
- (ii) The total weight of deposit formed on the feed-arm wall, W_D , at the end of test.

By plotting, in log-log form, the end-of-test increase in wall temperatures, ΔTIW , against the weight of deposit, W_D , for each test, an empirical linear relationship between the two parameters has been identified:

$$W_D = Y(\Delta TIW)^Z \quad \dots (1)$$

The value of Y is 1.82 and that of Z is 1.0, resulting in a linear relationship. This compares with the near quadratic form of relationship (i.e. $W_D \propto (\Delta TIW)^{2.2}$) found in the full-scale IFAR. The reason

for the differing exponents in the expression is obscure. One supposition is that the lower sandbath temperature of the MIFAR (400°C versus 540°C) has resulted in different heat-transfer characteristics between the sandbath and the feed-arm. However, there could well be other consequences of reducing scale.

The relationship has been used to convert the ΔT_{IW} recorded during the test to the equivalent W_0 , so generating a picture of the build-up of deposit as a function of duration (Figures 2 - 4). Now, assuming that deposition occurs only on the directly heated surface of 7.2cm^2 area, deposition rates have been calculated for each test (Table 2).

The main points are as follows:

- (1) The form of the curves confirms our earlier findings as to the nature of the deposition process; namely, it comprises three distinct phases:
 - A finite, variable-duration "induction period", during which no significant deposition occurs.
 - A period of near-constant deposition rate.
 - In some tests, a decrease in deposition rate towards the end of test.
- (2) Deposition rates span a factor of 25. The sweetened fuels (excluding off-grade Fuel A) encompass the range $0.1 - 0.5 \text{ mg cm}^{-2}\text{h}^{-1}$ and the hydrotreated fuels are all less than $0.05 \text{ mg cm}^{-2}\text{h}^{-1}$.
- (3) The highest deposition rate was that of the off-grade Fuel A, which was consistent with its high metal content. However, addition of MDA restored this high rate to that more typical for a sweetened fuel.

DISCUSSION

The nature of the deposition process

The graphs of the temporal evolution of deposits on the feed arms (Figure 2 - 4) show features identical to those in the IFAR study⁴, i.e. the three main phases in the deposition process noted above,

- Finite hold-up or induction period, during which little or no deposition is detected. This corresponds to the low deposition rate on a clean steel surface.

Followed by:

- A higher constant rate of deposition on a fouled surface.

Ultimately

- A reduction in deposition rate due to the insulating effect of the cumulative deposit.

However, the current studies, with the large suite of fuels, have given a much clearer insight into the deposition process. Examination of the data reveals an obvious link between the length of the induction period (r_{ip}) and the post-induction deposition rate (r_p); i.e. the less stable a fuel is, the shorter its induction period and the higher its deposition rate. In fact, it is reasonable that there should be a relationship between these two parameters; the reciprocal induction period ($1/r_{ip}$) is a measure of fuel deposition rate on a clean metal surface, whereas the post-induction rate is a measure of deposition rate on a fouled surface. In Figure 5, the plotting of deposition rate versus $1/r_{ip}$ yields a straight line passing through the origin, illustrating the relationship between two measures of deposition. The data can be interpreted further, by making certain assumptions. Examination of the W_d versus duration plots suggests that the induction period is the time taken for 5 mg of deposit to build up. From this, an estimation can be made of the relative fuel deposition rates on a clean surface versus those on a lacquered one; the ratio obtained is 1:4.

The influence of MDA

The mechanism by which the metal deactivator additive (MDA) affects fuel performance can be resolved into two components:

- Metal chelation, the claimed role of the additive, whereby dissolved metals within the fuel are rendered catalytically inactive. In this mode, bulk fuel reactivity is affected, thus increased chelation is manifested as a decrease in deposition rate.
- Metal passivation, in which the MDA adsorbs onto and, thereby, modifies a clean metal surface, thus inhibiting formation of the first layer of deposit. Increased passivation is evident from an increase in induction periods.

These feed-arm studies have provided an excellent illustration of the above mechanisms. Consider the test sequence 1 - 4 (Figure 2 - 4), in which an off-grade fuel (Fuel A) contaminated with catalytic metal is progressively doped with higher concentrations of the MDA additive (0, 5.7 and 12 mg l⁻¹). (i) The base fuel gave the highest deposition rate 1.1 mg cm⁻² h⁻¹ and the shortest induction period of 3 hours. (ii) At 5.7 mg l⁻¹, MDA is present in excess relative to the metal contamination (0.25 mg l⁻¹ of MDA would be required). Thus, all metals are chelated and the deposition rate decreases to 0.3 mg cm⁻² h⁻¹ via the chelation mechanism. However, in tandem, the induction period increases from 3 to 8 hours via the passivation mechanism. (iii) At 12 mg l⁻¹ there can be no extra benefit from chelation over and above that seen at the 5.7 mg l⁻¹ level, which was already an excess of MDA. In consequence, the deposition rate remains essentially unaffected. However, this additional MDA can affect the passivation mechanism and increase the induction period from 8 to 20 hours.

From our previous work⁴ using metal-free fuel to avoid the chelation mechanism, it can be estimated from the induction period data that deposition rates on a clean steel surface are reduced by two-thirds by the MDA passivation associated with the 5.7 mg l⁻¹ doping level.

Comparing the MIFAR with other measures of thermal stability

A major aim of the research programme was to predict fuel performance within the MIFAR from compositional data, and to relate the performance to other thermal stability rigs. Six potential predictors of fuel thermal stability were considered:

- (1) Radical initiation rate (FOT)
- (2) JFTOT breakpoint
- (3) JFTOT carbon deposit determination
- (4) Oil-cooler rig (i.e. STHTR) data
- (5) Fuel sulphur content
- (6) Total acid content (TAC) via ion-exchange

Accordingly, MIFAR test results in the form of deposition rates were correlated with these other measures. The resultant statistical information is illustrated in Table 3 and the correlation graphs in Figures 6 and 7.

Two striking features can be observed from the statistics:

- (1) The lack of a significant correlation between the oil-cooler rig and the MIFAR (correlation confidence is well below the significant level of 95%)
- (ii) The superiority of all the analytically derived predictors (i.e. sulphur, R_i and TAC), when compared to rig-based tests, in forecasting MIFAR deposition rates.

In fact these two points are probably related. The MIFAR, in its current configuration, simulates a fuel system that is not subject to wing tank heating. Thus, the fuel is not resident in any heated component for any length of time, and as a consequence one would expect deposition to be influenced by fuel chemistry in a straightforward manner, i.e. oxidation followed by reaction of intermediates with fuel polar species (acids and sulphur compounds). It is seen that the statistical data are in accord with such a mechanism. The poor correlation with the STHTR may well relate to the more complex chemistry associated with the multi-stage heating system of the rig whereby the fuel is pre-heated in a simulated wing tank for a comparatively long residence time (ca. 1 hour) before encountering the test section.

The poor correlation of the MIFAR with either JFTOT measure could result from the JFTOTs' lack of realism in utilising a laminar fuel flow condition and thus not responding solely to fuel chemistry⁷.

Overall, the best prediction of fuel thermal stability in both the large-scale rigs, i.e. the MIFAR and STHTR, is given by total acid content (TAC) via ion-exchange chromatography⁸.

CONCLUSIONS

- A half-scale injector feed-arm fouling rig, the MIFAR, provides clear confirmation of the deposition mechanisms first observed in full-scale

rig (i.e. the IFAR) measurements, namely, the three distinct deposition phases of induction, constant rate deposition and tail-off. However, working with a large suite of fuels enables the mechanism to be resolved at a greater level of detail. In particular, relationships have been drawn up between fuel deposition on a clean steel surface (estimated from the induction period length) and deposition on a fouled surface (post induction).

- MIFAR data provide an excellent illustration of the mode of action of the two mechanisms by which the approved thermal-stability-enhancing additive MDA affects fuel-deposition tendency: metal chelation and metal passivation. Chelation is measured as a change in the post-induction deposition rate, whereas passivation is measured in terms of the length of the induction period.
- Simple chemical composition parameters are superior to other measures for predicting the thermal stability performance of fuels in the MIFAR. These three parameters, radical initiation rate, fuel total sulphur and total acid content (TAC), are in accord with our current understanding of the chemistry of the degradation mechanism. TAC by ion-exchange chromatography is considered the best measure.
- The poor MIFAR/STHTR correlation suggests that the more complex heating stages within the STHTR have a significant effect on the chemistry of the decomposition process.

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Table 1
Inspection properties of fuels used in the MIFAR feeding studies

FUEL	A	B	C	D	E	F	G	H	I	J
PROCESS TYPE	SWEETENED	MERCK SWEETENED	MERCK SWEETENED	-50/50 STRAIGHT RUN/ HYDROCRACKED	MERCK SWEETENED (FUEL F) +12v UNTREATED LCCO	MERCK SWEETENED	MERCK SWEETENED	HYDROCRACKED PRODUCT	HYDROTREATED	HYDROTREATED
AROMATICS, Iv	18.9	19.2	19.2	18.4	27.7	17.5	17.4	8.6	16.0	14.7
OLEFINS, Iv	0.7	0.3	0.8	0.2	0.4	0.5	0.3	0.4	<1	0.4
MERCAPTAN SULPHUR, Iv	0.0002	0.0003	0.0005	0.0004	0.0008	0.0017	0.0002	0.0001	-	0.0001
TOTAL SULPHUR, Iv	0.14	0.03	0.10	0.01	0.30	0.21	0.133	0.013	0.002	0.004
ACTIVITY, mgKOH s ⁻¹	0.001	0.001	<0.001	0.007	0.003	0.003	0.001	0.001	0.004	0.001
*Total Acids, mg l ⁻¹	-	100	123	112	273	153	281	27	47	18
Distillation										
IBP, °C	163	151	148	153	154	141	147	171	155	160
50%, °C	166	203	190	197	223	194	180	210	200	199
FDB, °C	265	250	252	256	250	260	259	278	259	263
Density, kg l ⁻¹	0.8078	0.8110	0.7909	0.8032	0.8214	0.7960	0.7878	0.8033	0.7960	0.8016
Copper, µg l ⁻¹	47	2	7	<2	53	16	<2	2	2	<2
Antioxidant, mg l ⁻¹	Nil	Nil	Nil	18	Nil	Nil	Nil	20	20	20
JFTOT Breakpoint, °C	250	285	265	280	245	250	285	305	285	285

* Total Acid Content, TAC, extracted by ion exchange chromatography

Table 2
Comparison between MIFAR deposition rates and some other thermal stability indices

MIFAR Test no.	Fuel	MIFAR deposition rate mg cm ⁻² h ⁻¹	IFAR deposition rate mg cm ⁻² h ⁻¹	Single tube rig ΔHTC, °C h ⁻¹	JFTOT breakpoint, °C	JFTOT carbon deposit, µg	Radical initiation rate mol l ⁻¹ s ⁻¹ x 10 ⁷
1,2	A	1.04, 1.18	-	0.33	250	-	26.9
3,4	A + MDA 5.7 ppm, 12 ppm	0.31, 0.50	-	-	-	-	-
5,6	B	0.29, 0.37	0.43	1.3	285	143	2.5
7,8	C	0.18, 0.36	0.43	0.6	265	138	5.8
9	D	0.15	0.47	1.9	290	71	4.9
10	E	0.41	0.63	12.3	245	553	4.9
11,12	F	0.11, 0.10	-	1.3	250	307	6.3
13	G	0.22	-	5.4	285	87	0.5
14	H	0.046	-	0.2	305	59	0.70
15	I	0.049	-	0.19	285	54	0.93
16	J	0.046	-	0.002	285	25	0.76

Table 3

The correlation of MIFAR deposition rates with some other thermal stability indices

Test	Correlation Confidence, %	R	MSE*	Gradient [§]	Intercept [§]
$R_i, 10^{-7} \text{ mole l}^{-1} \text{ s}^{-1}$	99.7	0.730	0.106	$0.62 \pm 27\%$	$-1.0 \pm 12\%$
JFTOT, B.P., °C	95.5	0.542	0.160	$-7.9 \pm 45\%$	$1.8 \pm 46\%$
STHTR, $\Delta H_{TC}, \% \text{ h}^{-1}$	85.4	0.409	0.189	$0.21 \pm 64\%$	$-0.66 \pm 18\%$
S, % M	48.2	0.620	0.140	$0.41 \pm 37\%$	$-0.16 \pm 19\%$
# JFTOT, C.D. μg	96.3	0.601	0.090	$0.58 \pm 41\%$	$-2.0 \pm 25\%$
# TAC, mg l^{-1}	99.9	0.843	0.049	$0.77 \pm 20\%$	$-2.39 \pm 13\%$

+ MSE: Mean square error, |R| : Correlation Coefficient

§ Values in the expression

$$\log_{10} (\text{MIFAR}) = \text{Intercept} + \text{Gradient} * \log_{10} (\text{Test index})$$

Data set for these indices comprise 12 measurements. All others 14 measurements

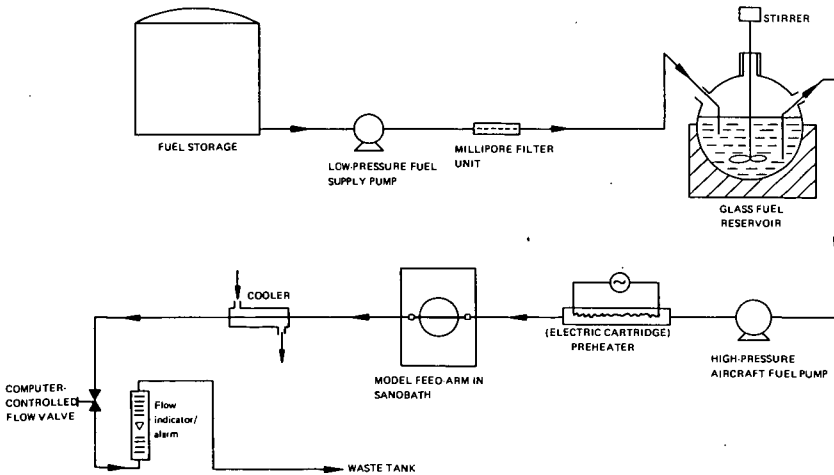


FIG. 1 - Schematic diagram of the Mini Injector Feed-Arm Rig (MIFAR)

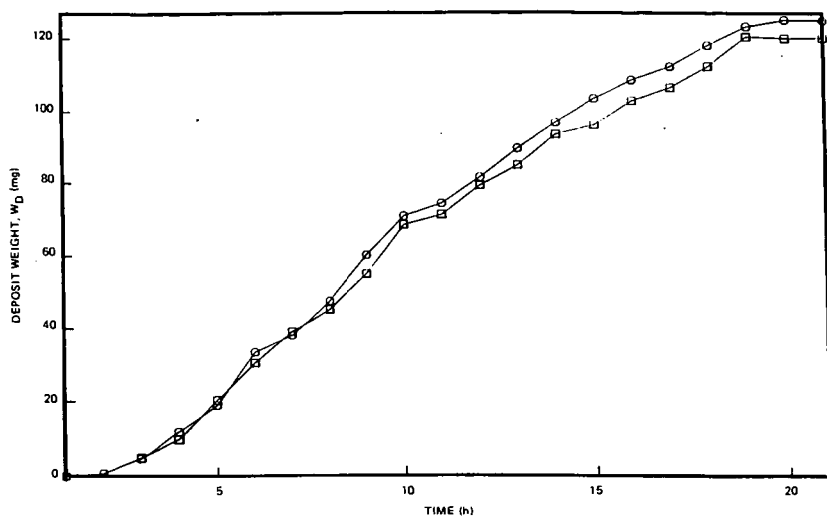


FIG. 2 — The evolution of feed-arm deposition for Fuel A, Test 2

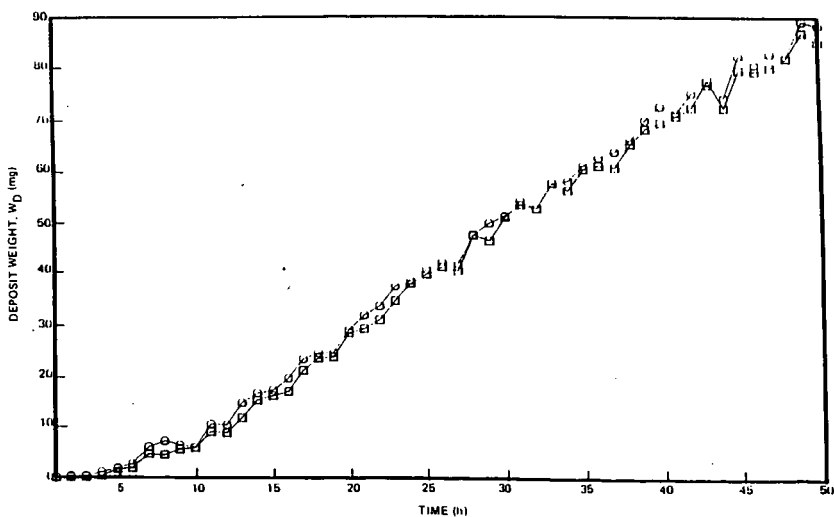


FIG. 3 — The evolution of feed-arm deposition for Fuel A + 5.7 mg l⁻¹ MDA

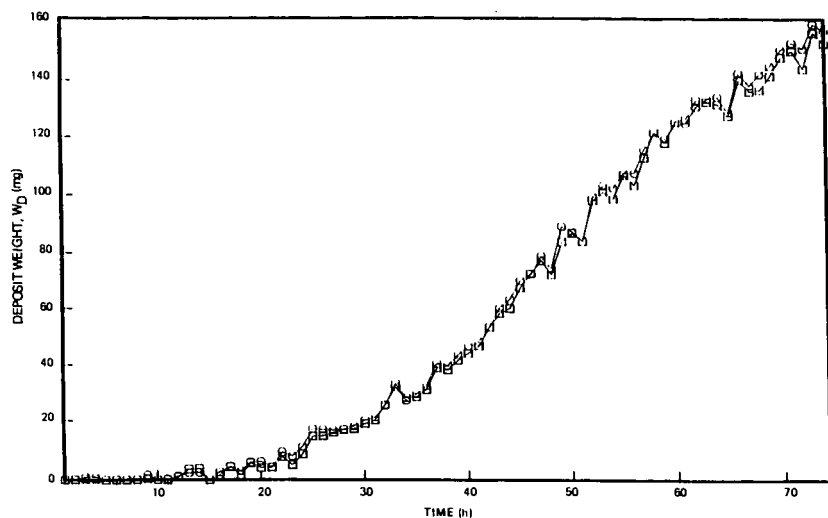


FIG. 4 - The evolution of feed-arm deposition for Fuel A + 12 mg l⁻¹ MDA

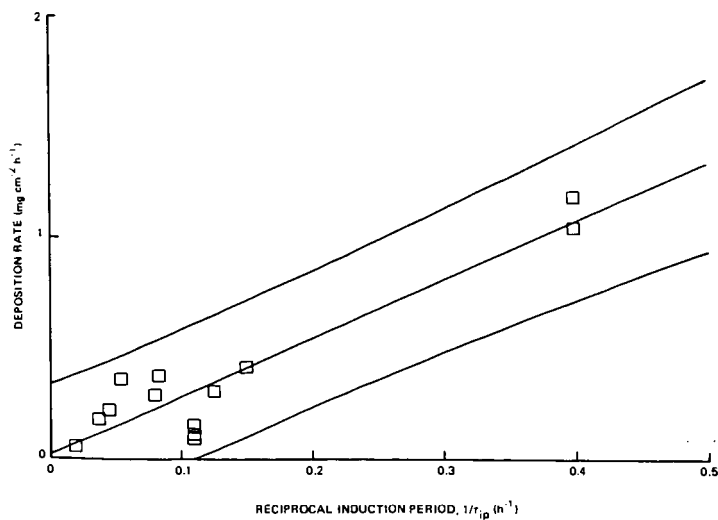


FIG. 5 - The relationship between feed-arm deposition rate and induction period

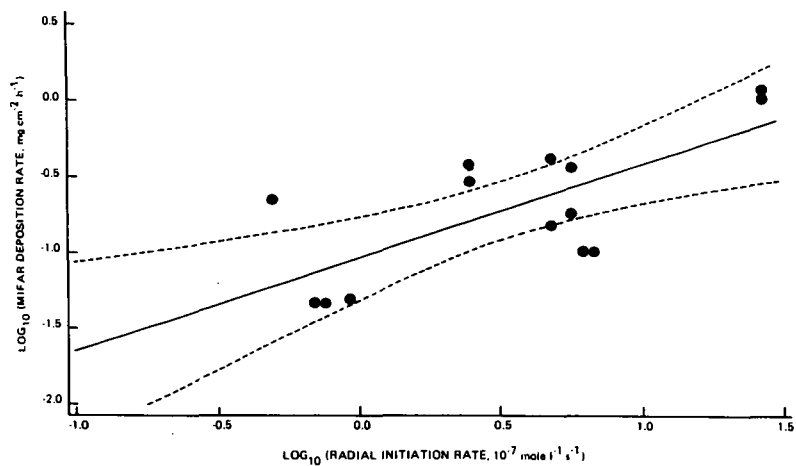


FIG. 6 — The correlation between feed-arm deposition rate in the MIFAR and fuel radical initiation rate

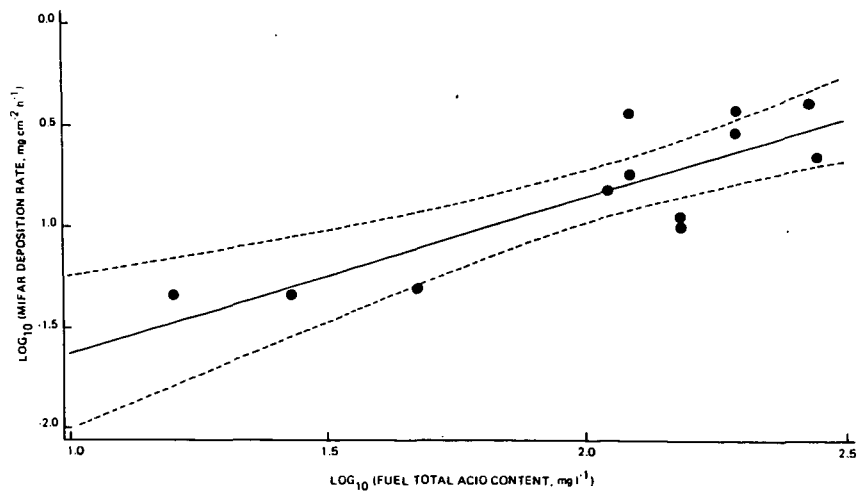


FIG. 7 — The correlation between feed-arm deposition rate in the MIFAR and fuel total acid content